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THE CONSTITUENTS

OF

OLIVE BARK

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LXXXIV.—*The Constituents of Olive Bark.*

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The bark of the olive tree, *Olea Europaea*, Linné, is reputed to possess medicinal properties similar to those of the leaves, but, with the exception of the observation that, like other parts of the plant, it contains mannitol, nothing appears to have been ascertained respecting

the character of its constituents. It may be noted, however, that from a so-called gum-resin, which excludes spontaneously from the bark of the olive tree in hot countries, a crystalline substance, designated olivil, was isolated many years ago. This substance which, as our investigation has shown, does not occur in the bark, has most recently been examined by Körner and Vanzetti (*Atti R. Accad. Lincei,* 1903, [v], **12**, i, 122), who state that, when anhydrous, it possesses the formula $C_{20}H_{24}O_7$ and melts at 142·5°.

In connexion with our investigation of olive leaves, it has been deemed desirable also to examine the constituents of the bark of the olive tree, and the results obtained are recorded in this communication.

Experimental.

The material employed in this investigation consisted of the air-dried bark of *Olea Europaea*, Linné, which had been collected for us during the early spring in the neighbourhood of Ventimiglia, on the Italian Riviera.

A portion of the bark was first tested for the presence of an alkaloid, but with a negative result.

Fifty grams of the ground bark were then successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 35—50°)	extracted	0·32	per cent.
Ether	,,	3·76	,,
Chloroform	,,	6·30	,,
Ethyl acetate	,,	4·56	,,
Alcohol	,,	15·30	,,
	Total	30·24	,,

For the purpose of a complete examination, a quantity (34·92 kilograms) of the ground bark was extracted by continuous percolation with hot alcohol. One kilogram of the resulting viscous extract, containing 875 grams of extracted material, was then mixed with water and distilled with steam, but no volatile product was obtained. The dark-coloured, aqueous liquid in the distillation flask was separated by filtration, while still hot, from a relatively small amount of dark green resin (*A*), and the latter thoroughly washed with boiling water. The combined filtrate and washings were then diluted to about 10 litres and allowed to cool, when a large amount of a heavy, brown, syrupy product (*B*) was deposited. This was separated, and freed from substances soluble in cold water, after which the combined aqueous liquid and washings (*C*) were concentrated to about 2 litres.

Examination of the Green Resin (*A*).

This resin, which amounted to 54 grams, was a dark green, wax-like solid at the ordinary temperature, but when heated to about 80° it melted to an oil. After being mixed with purified sawdust, it was successively extracted in a Soxhlet apparatus with the following solvents: petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

Isolation of a New Monocarboxylic Acid, $C_{34}H_{67}\cdot CO_2H$.

The petroleum extract of the resin was a dark green, wax-like solid, and weighed 28·6 grams. It was dissolved in ether, and the ethereal liquid shaken with a solution of sodium carbonate, when a quantity of a green, flocculent precipitate was formed. The ethereal and aqueous liquids were separated from the precipitate by filtration, when, on acidifying the latter liquid, it was found to contain no insoluble acid. The solid was then well washed with ether, warmed with dilute sulphuric acid, and the liberated acid isolated by means of chloroform. On removing the solvent, a green residue was obtained, which was distilled under diminished pressure. The light brown distillate solidified on cooling, and was crystallised from ethyl acetate, with the use of animal charcoal. Small, colourless leaflets were thus obtained which melted at 69—70°, and this melting point was not altered by repeated crystallisation. Two different preparations of this substance were analysed:

0·1036 gave 0·3071 CO_2 and 0·1242 H_2O. C = 80·5; H = 13·3.
0·1033 „ 0·3049 CO_2 „ 0·1246 H_2O. C = 80·5; H = 13·4.
$C_{35}H_{68}O_2$ requires C = 80·8; H = 13·1 per cent.

This *acid* would thus appear to possess the formula $C_{35}H_{68}O_2$, and, since no substance of this formula has previously been described, it is apparently a new compound. It behaves towards bromine as a saturated compound, and yields *sodium*, *potassium*, and *ammonium* salts, which are insoluble in water. It is only sparingly soluble in cold chloroform or in boiling alcohol, and a warm solution of it in the former solvent was found to be optically inactive. It was not possible to titrate accurately this acid, or any of the analogous acids subsequently described, on account of their sparing solubility and the flocculent character of their insoluble salts.

The *ethyl* ester was prepared by means of ethyl alcohol and sulphuric acid. After being freed from traces of unchanged acid, it crystallised in leaflets melting at 63°:

0·1140 gave 0·3386 CO_2 and 0·1390 H_2O. C = 81·0; H = 13·5.
$C_{34}H_{67}\cdot CO_2\cdot C_2H_5$ requires C = 81·0; H = 13·1 per cent.

Isolation of a New Monocarboxylic Acid, $C_{24}H_{45}\cdot CO_2H$.

The green, ethereal liquid, from which the above-described acid had been removed by means of sodium carbonate, was shaken with a solution of sodium hydroxide. This treatment caused the separation of a precipitate similar to that previously produced by sodium carbonate, but the amount was somewhat larger. The alkaline, aqueous liquid obtained in this case also yielded nothing on acidification. The precipitate apparently consisted of a sodium derivative. It was therefore warmed with dilute sulphuric acid, and the mixture extracted with chloroform, when, on evaporating the chloroformic liquid, a green, wax-like solid was obtained. This was crystallised from ethyl acetate, with the use of animal charcoal, when it separated in small, colourless leaflets, which melted at 79°, and this melting-point was not altered by further crystallisation.

0·1175 gave 0·3406 CO_2 and 0·1304 H_2O. C = 79·1 ; H = 12·3.
0·1106 ,, 0·3216 CO_2 ,, 0·1236 H_2O. C = 79·3 ; H = 12·4.
$C_{25}H_{46}O_2$ requires C = 79·3 ; H = 12·2 per cent.

Notwithstanding the fact that this substance cannot be removed from its solution in ether by means of sodium carbonate, a property which was confirmed when working up a second portion of extract from the bark, it must be regarded as a carboxylic acid, for it crystallises unchanged from acetic anhydride after being boiled for some time with this reagent, exhibits an acid reaction to phenolphthalein, and yields an ethyl ester. Since no compound of the formula $C_{25}H_{46}O_2$ has hitherto been described, it must, moreover, be regarded as a new *acid*. It is very sparingly soluble in alcohol, behaves towards bromine as a saturated substance, and, when dissolved in chloroform, is optically inactive.

The *ethyl* ester was prepared in the usual manner by means of ethyl alcohol and sulphuric acid. It was dissolved in chloroform, and freed from unchanged acid by means of sodium hydroxide, after which it was crystallised from ethyl acetate, when it separated in glistening plates melting at 66·5°:

0·0946 gave 0·2775 CO_2 and 0·1060 H_2O. C = 80·0 ; H = 12·4.
$C_{24}H_{45}\cdot CO_2\cdot C_2H_5$ requires C = 79·8 ; H = 12·3 per cent.

Isolation of Ipuranol, $C_{23}H_{38}O_2(OH)_2$.

The original ethereal liquid, which had been shaken with solutions of sodium carbonate and hydroxide, was washed with water, when a deep green, alkaline, aqueous liquid was obtained, which evidently contained a large amount of chlorophyll in combination with sodium. This solution was acidified with sulphuric acid, when the chlorophyll

was precipitated. On attempting to extract the latter with ether, a quantity of solid remained undissolved, and was collected on a filter. This solid was washed by boiling it with several successive portions of ether, and then dissolved in boiling alcohol, in which it was very sparingly soluble. The alcoholic solution, which was green, was decolorised by means of animal charcoal, when, on allowing it to cool, a small quantity (less than 0·1 gram) of a colourless solid separated in the form of small, very flocculent tufts of extremely fine needles. This substance was not very distinctly crystalline, but was obtained more definitely so on cooling its solution in dilute pyridine. In order to obtain it in greater amount, a further large quantity of extract from the bark was employed. The substance, even when pure, does not melt sharply, but fusion takes place between 285° and 290°, some gas being evolved from the melted substance.

0·0944 gave 0·2510 CO_2 and 0·0907 H_2O. C = 72·6 ; H = 10·7.
0·1034 ,, 0·2752 CO_2 ,, 0·0984 H_2O. C = 72·6 ; H = 10·6.
$C_{23}H_{40}O_4$ requires C = 72·6 ; H = 10·5 per cent.

Although no compound of the formula $C_{23}H_{40}O_4$ has hitherto been brought to notice, a substance having this composition was recently isolated in small amount in these laboratories from the stems of *Ipomoea purpurea*, Roth (*Amer. J. Pharm.*, in the press), and the two preparations have been found to be identical. This substance, with reference to the source from which it first was obtained, has received the designation *ipuranol*.

Diacetylipuranol, $C_{23}H_{38}O_4(CO{\cdot}CH_3)_2$.—A small quantity of ipuranol was boiled with acetic anhydride, when it very slowly dissolved. On concentrating the solution and allowing it to cool, *diacetylipuranol* separated in well-defined, glistening leaflets, which melted at 160° :

0·1124 gave 0·2875 CO_2 and 0·0949 H_2O. C = 69·8 ; H = 9·4.
$C_{23}H_{38}O_4(CO{\cdot}CH_3)_2$ requires C = 69·8 ; H = 9·5 per cent.

The identity of the substance, $C_{23}H_{40}O_4$, from olive bark with ipuranol (from *Ipomoea purpurea*) was further confirmed by a comparison of their respective acetyl derivatives. Since ipuranol yields a diacetyl derivative, it evidently contains two hydroxyl groups, and, inasmuch as it gives a sodium derivative when treated with sodium hydroxide, one at least of these groups must possess phenolic properties. Diacetylipuranol, however, when dissolved in chloroform, does not react with aqueous alkalis.

Ipuranol is quite insoluble in petroleum, and nearly so in ether. It could not therefore have been present in the petroleum extract of the resin in a free state, and, as it was obtained from the chlorophyll after the latter had been removed from the ethereal solution of the petroleum extract in the form of a compound with the alkali, it

probably existed in the bark in combination with some constituent of the chlorophyll which suffered hydrolysis whilst in solution in the dilute aqueous sodium hydroxide.

The original ethereal liquid from which the ipuranol had been obtained was evaporated, and the residue boiled for some time with an alcoholic solution of an excess of potassium hydroxide. The alcohol was then removed, water added, and the liquid extracted with ether. A small quantity of a flocculent precipitate collected in the lower portion of the ethereal layer, which was found to consist of an insoluble potassium salt. The acid obtained from this salt crystallised from ethyl acetate in plates melting at 67°, but the amount was not sufficient for analysis. The alkaline aqueous liquid was separated and found to contain, besides formic and butyric acids in small amount, only chlorophyll and amorphous matter. The ethereal solution of the unsaponifiable substances was bright yellow. The solvent was removed, and the residue fractionally crystallised from absolute alcohol, when a very small amount of a substance was obtained, which, after distillation under diminished pressure, crystallised in small plates melting at 74—75°:

0·0804 gave 0·2503 CO_2 and 0·1071 H_2O. C = 84·9; H = 14·8.

$C_{35}H_{72}$ requires C = 85·4; H = 14·6 per cent.

This substance was thus identified as pentatriacontane.

The mother liquors from this hydrocarbon yielded a substance which, after several recrystallisations, separated from a mixture of ethyl acetate and dilute alcohol in long, flattened needles, which melted at 134°. After being distilled under diminished pressure, and again crystallised as before, the substance melted at 136°:

0·1076, on drying at 110°, lost 0·0053 H_2O. H_2O = 4·9.

0·0917 gave 0·2804 CO_2 and 0·1008 H_2O. C = 83·4; H = 12·2.

$C_{27}H_{46}O,H_2O$ requires H_2O = 4·5.

$C_{27}H_{46}O$ requires C = 83·9; H = 11·9 per cent.

The substance therefore was evidently a phytosterol, and, when dissolved in chloroform and treated with acetic anhydride and sulphuric acid, it yielded the colour reaction characteristic of these alcohols. It differed, however, in appearance from the phytosterols usually obtained, since it crystallised in long, flattened needles, and not in plates. A determination of its optical rotatory power gave the following result:

0·3965 of anhydrous substance, dissolved in 25 c.c. of chloroform gave $[\alpha]_D$ $-1°7'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-35·2°$.

The melting point and rotation of this phytosterol agree approximately with those of sitosterol (*Zeitsch. physiol. Chem.*, 1902, **34**, 461), which melts at 137° and has $[\alpha]_D$ $-33·9°$. The acetate of the phyto-

sterol from olive bark, however, crystallised in silky laminæ melting at 119·5°, and this melting point could not be raised, whereas sitosteryl acetate melts at 128°. It would appear therefore that the two alcohols are not identical.

Ethereal Extract of the Resin.

Isolation of a New Monocarboxylic Acid, $C_{34}H_{69}\cdot CO_2H$.

The portion of the resin removed by ether amounted to 13 grams. As originally obtained, it consisted of a green, ethereal solution containing a quantity (about 4 grams) of a light-coloured precipitate. The latter was collected on a filter and well washed with ether, after which it was dissolved in a large volume of hot alcohol, the solution decolorised by means of animal charcoal, and allowed to cool. A quantity of a white, amorphous solid then separated. This was collected on a filter, again dissolved in hot alcohol, and allowed to separate, but it still remained amorphous. The solid substance, which melted at 90°, was therefore dried and then distilled under a pressure of 13 mm., when it passed over up to 365° without decomposition. The distillate was crystallised from ethyl acetate, from which it separated in small, colourless leaflets melting at 92°:

0·0975 gave 0·2872 CO_2 and 0·1189 H_2O. C = 80·3; H = 13·5.
0·0855 ,, 0·2524 CO_2 ,, 0·1043 H_2O. C = 80·5; H = 13·5.
$C_{35}H_{70}O_2$ requires C = 80·5; H = 13·4 per cent.

This substance was an *acid*, as was evident from its behaviour to phenolphthalein. It yields *sodium*, *potassium*, and *ammonium* salts, which are flocculent, insoluble solids, and readily gives an *ethyl* ester. Since no substance of the formula $C_{35}H_{70}O_2$ has heretofore been described, it must, moreover, be regarded as a new compound. The acid is only sparingly soluble in most of the usual organic solvents when cold, and, so far as could be observed with a dilute chloroformic liquid, it is optically inactive. It would not appear probable, however, that it is a normal fatty acid, since it is absolutely insoluble in light petroleum. It is also more soluble in boiling alcohol than the acid $C_{35}H_{68}O_2$, which was obtained from the petroleum extract of the resin.

A small quantity of the *ethyl* ester was prepared. This crystallised in leaflets, which were rather larger than those of the corresponding acid, and melted at 87°.

Isolation of a New Monohydric Alcohol, $C_{35}H_{67}\cdot OH$.

The above described acid, melting at 92°, did not represent the whole of that portion of the ethereal extract of the resin which was

sparingly soluble in this solvent. It was evident that a mixture of other substances of lower melting point was present in the mother liquors together with a trace of a compound melting above 250°, which will be referred to later. A further and much larger quantity of the sparingly soluble material was obtained, and submitted to fractional distillation under diminished pressure, when the following fractions were collected: below 250°, 250—290°, 290—320°, 320—360°/13 mm. The last two fractions, on crystallisation, yielded a product which melted at 87°, and, on analysis, was found to consist essentially of the above-described acid (m. p. 92°). The portion boiling below 250° was only small in amount and was not examined, but the fraction 250—290°/13 mm. yielded a product which crystallised from ethyl acetate in flattened needles melting at 70°, and this melting point was not altered by repeated crystallisation. On analysis, it gave the following result:

0·0907 gave 0·2778 CO_2 and 0·1136 H_2O. C = 83·5; H = 13·9.
$C_{35}H_{68}O$ requires C = 83·3; H = 13·5 per cent.

This *substance* is evidently identical with the compound, melting at the same temperature, which was subsequently isolated from the portion of the ethereal extract of the resin which was more readily soluble in this solvent, although the percentage of carbon found is a trifle too high. It may be noted that its formula differs by the elements of one molecule of water from that of the above-described acid melting at 92°, but it is much more soluble than the latter in chloroform.

The boiling point of the fraction, from which this substance was obtained, shows that the molecular weight of the compound cannot be twice that indicated by the above formula. The substance therefore contains only one oxygen atom, but, notwithstanding this fact, it can be removed completely from its solution in chloroform or benzene by means of sodium hydroxide, an insoluble, flocculent *sodium* compound being formed. The slight phenolic properties of the compound may be accounted for by regarding it as a tertiary alcohol and by its possessing such a high molecular weight. An acetyl derivative could not be obtained from it, and this also indicated that it did not contain a primary or secondary alcoholic grouping. Since no compound of the formula $C_{35}H_{68}O$ has previously been described, it must, moreover, be regarded as a new substance. When dissolved in chloroform, it does not absorb bromine, and would therefore appear to possess a cyclic structure.

The original alcoholic mother liquors, obtained after the preliminary purification by means of animal charcoal, of that portion of the ethereal extract of the resin which was sparingly soluble in this

solvent contained, as previously stated, a very small amount of a substance melting above 250°. They were therefore evaporated to dryness, and the residue extracted with boiling benzene. The small amount of material which remained undissolved by this treatment was crystallised from dilute pyridine, after which it melted at 285—290°, and by conversion into its acetyl derivative (m. p. 160°) was identified as ipuranol. This trace of ipuranol, obtained from the ethereal extract of the resin, had evidently existed in the plant in the free state.

Isolation of a New Monocarboxylic Acid, $C_{29}H_{57}\cdot CO_2H$.

The original ethereal filtrate from the sparingly soluble precipitate, the examination of which has just been described, was shaken with a solution of ammonium carbonate. This caused the separation of a flocculent *ammonium* salt, which was collected on a filter and well washed with ether. The aqueous portion of the filtrate from this precipitate yielded nothing on acidification. The precipitate was treated with dilute sulphuric acid, and the liberated acid extracted by means of chloroform. On removing the solvent, a green, wax-like solid, was obtained, which was distilled under diminished pressure, after which it was crystallised from ethyl acetate with the use of animal charcoal. The acid then separated in small, glistening leaflets melting at 82°, and when again crystallised from ethyl acetate its melting point was raised to 84°:

0·0938 gave 0·2748 CO_2 and 0·1104 H_2O. C = 79·9; H = 13·1.

After another crystallisation, the melting point of the substance remained unchanged, and it was again analysed:

0·0950 gave 0·2784 CO_2 and 0·1103 H_2O. C = 79·9; H = 12·9.

$C_{30}H_{58}O_2$ requires C = 80·0; H = 12·9 per cent.

As no compound possessing the formula $C_{30}H_{58}O_2$ has previously been described, the substance melting at 84° must be regarded as a new *monocarboxylic acid*. Its empirical formula would appear to indicate that it belongs to the oleic acid series, but, when dissolved in chloroform, it does not absorb bromine, and may therefore be considered to possess a cyclic structure.

The *ethyl* ester of this acid was prepared in the usual manner, and, after being freed from traces of unchanged acid, was found to melt at 75°. It crystallised from ethyl acetate in glistening plates, which dried to a parchment-like mat:

0·0939 gave 0·2766 CO_2 and 0·1114 H_2O. C = 80·3; H = 13·2.

$C_{29}H_{57}\cdot CO\cdot C_2H_5$ requires C = 80·3; H = 13·0 per cent.

The ethereal liquid, from which the above-described acid had been obtained in the form of its ammonium salt, was shaken with a solution

of sodium carbonate. Nothing was dissolved by this alkali, but a small amount of a flocculent precipitate separated, from which, however, no pure substance could be isolated.

The ethereal liquid was then shaken with a solution of sodium hydroxide, when a flocculent, insoluble sodium compound separated. The latter was treated with dilute sulphuric acid, and the liberated substance extracted by means of chloroform. On removing the solvent, a residue was obtained which contained a considerable amount of chlorophyll. It was purified by several distillations under diminished pressure, and finally by crystallisation from ethyl acetate, when colourless, flattened needles, melting at 70°, were eventually obtained:

0·0847 gave 0·2583 CO_2 and 0·1061 H_2O. C = 83·2; H = 13·9.
0·0984 ,, 0·3003 CO_2 ,, 0·1212 H_2O. C = 83·2; H = 13·7.
$C_{35}H_{68}O$ requires C = 83·3; H = 13·5 per cent.

This compound was identical with the previously-described substance of the same composition and melting point, which is probably a tertiary alcohol.

The final ethereal solution, which had been extracted by alkalis as above described, contained only a trace of amorphous, green substance.

Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.

The chloroform extract of the resin amounted to about 6 grams, and was evidently a complex mixture. It was shaken with aqueous alkalis, but no pure substance could be obtained from it.

The portion of material removed by ethyl acetate was very small. It consisted of resin together with a trace of *d*-mannitol, which had escaped extraction by water during the preliminary treatment.

The remaining small portion of the resin, which was soluble only in alcohol, consisted of a brown, amorphous product.

Examination of the Brown Resin (*B*).

This product, as first obtained, was a heavy, brown, viscid syrup. After being completely freed from substances soluble in cold water, it was dried on a water-bath, when it formed a somewhat soft, brown resin, amounting to 283 grams. This was dissolved in alcohol, and the solution evaporated on purified sawdust, after which the dry material was extracted successively in a large Soxhlet apparatus with ether, chloroform, ethyl acetate, and alcohol.

The amount of material removed by ether was very small. It was freed from a trace of substance soluble in petroleum, redissolved in ether, and then extracted with a solution of ammonium carbonate,

The aqueous, alkaline liquid thus obtained, after filtering, was acidified with sulphuric acid, a small quantity of precipitated tarry matter removed, and the solution then extracted many times with ether. The ethereal liquid, on evaporation, yielded a small, crystalline residue, which, after recrystallisation from alcohol, melted at 265°, and was identical with a compound which was subsequently obtained in larger amount from the aqueous liquid (*C*). No other crystalline substance could be obtained from the ethereal extract of the brown resin.

The chloroform extract of the brown resin was relatively small in amount, and, although exhaustively examined, it yielded nothing crystalline.

The ethyl acetate extract represented the greater part of the brown resin, but nothing could be separated from it. A large proportion of it was only sparingly soluble in ethyl acetate, and, in view of the possibility of this containing a glucosidic substance, it was freed from any traces of sugar and then heated with dilute alcoholic sulphuric acid. On evaporating the alcohol after this treatment, a quantity of a black resin was obtained, from which nothing could be isolated, but, after removing the sulphuric acid from the aqueous liquid, the latter yielded a small quantity of *d*-phenylglucosazone. It was thus evident that some material of a glucosidic nature was present in the ethyl acetate extract.

The remaining portion of the brown resin, which was soluble only in alcohol, amounted to about one-third of the whole. Its solution in alcohol dried to a hard, brown varnish. When treated with dilute alcoholic sulphuric acid, it yielded a quantity of dextrose, but the only other product was an amorphous resin.

Examination of the Aqueous Liquid (*C*).

Isolation of a New Phenolic Substance, Olenitol, $C_{14}H_{10}O_6$.

The concentrated aqueous liquid (*C*) was repeatedly extracted with ether, the combined ethereal liquids shaken with several successive portions of a solution of sodium carbonate, and the alkaline liquids then separately examined. The liquid obtained by the first extraction with sodium carbonate yielded, on acidification, a precipitate of a dark brown, heavy oil, and, when allowed to stand for some time, it also deposited a small amount of pale yellow crystals. The mixture was shaken with a small volume of ether, when apparently only the oil dissolved, and the crystals were then collected on a filter. The ethereal portion of the filtrate was then separated, but this was found to contain only a brown, oily product. A further small quantity of the crystalline substance was, however, obtained by repeatedly extracting the acid, aqueous liquid with ether,

The liquid obtained by shaking the ethereal extract of the aqueous liquid with a second portion of sodium carbonate solution also yielded a small amount of this crystalline substance, but all the subsequent extractions with this alkali gave only tarry products. The original ethereal liquid, after complete extraction with sodium carbonate, yielded only a brown, viscid syrup.

The different portions of the crystalline substance were mixed and recrystallised from alcohol, when it was obtained in short, yellow needles melting at about 265°. This product was found to be identical with the small amount of crystalline substance which had been obtained from the ethereal extract of the brown resin, as already described. The products from the two sources were therefore mixed and again crystallised from alcohol, after which the substance still melted at about 265°, although not quite sharply, some decomposition occurring. On drying at 110°, it was found to be anhydrous:

0·0988 gave 0·2220 CO_2 and 0·0338 H_2O. C = 61·3; H = 3·8.

As the amount of this substance available was not sufficient for another analysis, a further portion of it was obtained by working up a larger quantity of the original extract of the bark, and this, on analysis, gave the following result:

0·0988 gave 0·2216 CO_2 and 0·0327 H_2O. C = 61·2; H = 3·7.

$C_{14}H_{10}O_6$ requires C = 61·3; H = 3·6 per cent.

The properties of this substance do not agree exactly with those of any compound of the formula $C_{14}H_{10}O_6$ which has previously been described. It was thought, however, that it might possibly be identical with a substance prepared by A. Michael (*J. pr. Chem.*, 1887, [ii], **35**, 510) by the condensation of ethyl oxalate with resorcinol, which is stated to fuse at about 259°. A quantity of the latter substance was therefore prepared, but was found to differ totally in many of its properties from the compound from olive bark. The yellow, crystalline substance $C_{14}H_{10}O_6$ is therefore a new compound, and it is proposed to designate it *olenitol.*

Olenitol is slightly soluble in water, ether, or ethyl acetate, and somewhat more readily so in alcohol. Its dilute solution in water or aqueous alcohol is slightly yellow, and exhibits a pale blue fluorescence. When dissolved in cold sulphuric acid, olenitol gives a colourless solution, but its solution in alkalis is intensely yellow, and, when largely diluted, displays a violet-blue fluorescence. An aqueous solution of olenitol gives with ferric chloride an intense, moss-green colour.

Olenitol does not contain a carboxyl group, since its acetyl derivative is insoluble in cold aqueous alkalis. It must, therefore, be regarded as a phenolic compound. Methoxyl groups also do not appear to be

present, for the olenitol was recovered unchanged after being boiled for an hour with 70 per cent. sulphuric acid.

Acetylolenitol was prepared by boiling olenitol with acetic anhydride for half an hour. The anhydride was then decomposed by water, and the greater part of the acetic acid neutralised by sodium carbonate. Acetylolenitol then separated in a crystalline form, and, after recrystallisation from alcohol, was obtained in nearly colourless leaflets, melting at 130°. The amount of this derivative was, however, not sufficient for analysis.

The original aqueous liquid, which had repeatedly been extracted with ether, was shaken with many successive portions of amyl alcohol. This treatment removed about 80 grams of a product which was similar in appearance to the previously-described brown resin (*B*). It was exhaustively examined, and found to be a very complex mixture. All the products obtained from it were brown, very viscid syrups, which, when dissolved in boiling water, reduced Fehling's solution, but nothing crystalline could be obtained from them.

The aqueous liquid, after being freed from amyl alcohol by means of steam, was treated with an excess of a solution of basic lead acetate. A bulky, yellow precipitate was thus obtained, which was collected on a filter, well washed with boiling water, then suspended in water, and decomposed by hydrogen sulphide. The liquid filtered from the lead sulphide, when concentrated, formed a brown syrup, which appeared to contain a large amount of tannic matter, but the only crystalline substance that could be isolated from it was a trace of oxalic acid.

The filtrate from the basic lead acetate precipitate was deprived of lead, and concentrated under diminished pressure, when, on allowing it to stand for some time, it deposited a quantity (55 grams) of crystals. These were collected and recrystallised from dilute alcohol, after which they melted at 165° and were identified as *d*-mannitol:

0·1035 gave 0·1505 CO_2 and 0·0750 H_2O. C = 39·7; H = 8·0.

$C_6H_{14}O_6$ requires C = 39·6; H = 7·7 per cent.

The original syrupy filtrate from the *d*-mannitol readily reduced Fehling's solution, and evidently contained a large amount of sugar, for, when warmed with phenylhydrazine acetate, it yielded *d*-phenylglucosazone, which, when heated somewhat rapidly, melted at 217°.

The liquid was further tested for the presence of a glucoside, but only a black resin and a little furfuraldehyde were obtained.

Summary.

The results of this investigation may be summarised as follows:

The air-dried olive bark employed, on percolation with hot alcohol, yielded about 30 per cent. of its weight of extracted material, of which

61·5 per cent. was soluble in cold water. A further 32·3 per cent. could be dissolved by boiling water, but separated on cooling, whilst the remainder amounting to about 6·2 per cent., was quite insoluble in either cold or hot water.

The portion of the alcoholic extract which was dissolved by cold water contained an amount of *d*-mannitol equivalent to nearly 1·9 per cent. of the weight of air-dried bark, together with tannic matter, viscid, brown products, and a sugar which yields *d*-phenylglucosazone. It also contained a small amount of a new, crystalline phenolic substance, *olenitol*, $C_{14}H_{10}O_6$ (m. p. 265°), dilute solutions of which show a blue fluorescence. *Acetylolenitol* melts at 130°.

The portion of the alcoholic extract which was soluble in hot but not in cold water consisted for the most part of brown, resinous products, some of which yielded glucose on hydrolysis, but a small amount of olenitol was also obtained from them.

The material insoluble in water consisted chiefly of a mixture of new *monocarboxylic acids*, all of which crystallise from ethyl acetate in small leaflets. They have the following composition and properties: (1) an *acid*, $C_{34}H_{67}\cdot CO_2H$ (m. p. 69—70°), which yields an *ethyl* ester melting at 63°; (2) an *acid*, $C_{24}H_{45}\cdot CO_2H$ (m. p. 79°), the *ethyl* ester of which melts at 66·5°. Both of these acids are soluble in petroleum (b. p. 35—50°); (3) an *acid*, $C_{34}H_{69}\cdot CO_2H$ (m. p. 92°), which is insoluble in petroleum, and yields an *ethyl* ester melting at 87°; (4) an *acid*, $C_{29}H_{57}\cdot CO_2H$ (m. p. 84°), which yields an *ethyl* ester melting at 75°, and, like the preceding one, is insoluble in light petroleum. In addition to these acids, a *substance*, probably a *tertiary alcohol*, $C_{35}H_{68}O$ (m. p. 70°), was obtained, together with a small amount of pentatriacontane, $C_{35}H_{72}$ (m. p. 74—75°), a phytosterol, $C_{27}H_{46}O$ (m. p. 136°; $[\alpha]_D - 35\cdot 2°$), the acetate of which melts at 119·5°, and a very small amount of a *substance*, $C_{23}H_{38}O_2(OH)_2$ (m. p. 285—290°), which yields an *acetyl* derivative, $C_{23}H_{38}O_4(CO\cdot CH_3)_2$, melting at 160°. This last-mentioned substance is identical with a compound which has recently been isolated by Power and Rogerson from *Ipomoea purpurea*, and designated *ipuranol*.

In conclusion it may be noted that the constituents of olive bark are quite dissimilar to those of the leaves, as our investigations have shown that only three substances are common to both, namely, *d*-mannitol, sugar, and pentatriacontane. In view of the large percentage of fatty oil contained in the ripe fruit of the olive tree, it may also be considered remarkable that the bark should be devoid of even traces of the ordinary fatty acids.

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